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**ELECTRO-CHEMICAL-MECHANICAL, LOW STRESS,
AUTOMATIC POLISHING (ECMP) DEVICE (Preprint)**

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Electro-Chemical-Mechanical, low stress, automatic polishing (ECMP) device

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Abstract

This document describes a low stress automated polishing device that was developed to prepare titanium and nickel alloy samples for imaging with electron microscopy. The system uses pulsed electrochemical reactions within an alkaline electrolyte to generate a thin passivation layer on the surface of the sample, which is removed by the mechanical vibration of the system. This research documents the passivation layer development and removal for Ti-6Al-4V and nickel 718 samples subjected to varying electrical potential cycles and vibration polishing times. Results indicate applied cyclic potentials removed material faster than typical removal techniques. In addition, electron back scatter defraction data showed less subsurface sample damage using the electro-chemical-mechanical process compared to standard mechanical polishing.

1. Introduction

With growing use of advanced electron-optic microscopes and the evaluation of hybrid and novel material systems, surface preparation of samples is an increasingly vital component in specimen characterization. The state-of-the-art in surface preparation for titanium and nickel base superalloys usually involves mechanical polishing from a diamond saw cut surface to a 3 – 6 micron finish. The samples are then typically polished using 0.05 micron colloidal silica in a mechanical vibration system (Vibromet™) [1-3]. Damage to the surface or subsurface of the material can adversely impact image quality from traditional backscatter electron imaging techniques and data from electron back scatter diffraction (EBSD). For high strength titanium and nickel base superalloys, both of these techniques are widely used to characterize microstructures for inputs into models that predict mechanical response [4-6]. In addition, surface preparation steps are critical to the imaging of ceramic and hybrid materials involving ceramic components. Traditional sample preparation often liberate small precipitates and inclusions that damage matrix materials and other phases during final polishing of the samples. The resultant micro scratches are often very difficult to remove from the surface and can cause significant subsurface damage .

The use of surface techniques to form protective coatings on metallic surfaces has been well documented [7-12]. In electropolishing techniques, a negative potential is applied to the metallic surface and metal is removed by interaction with the electrolyte. This is typically done to prepare surfaces for manufacturing processes and/or imaging with electron optics. With anodizing techniques, titanium and other metal surfaces are subjected to an applied positive potential where they act as the anode in an electro-chemical process, resulting in the formation of an oxide layer on the metallic surface [9,10]. The anodic layer that forms on these materials has been characterized by many researchers and provides significant corrosion resistant properties [11,12]. In titanium alloys, stable TiO₂ surface oxide layers form dependent on the pH of the

electrolyte and the applied potentials. For titanium, researchers have shown TiO_2 is stable in pH values between 8 and 10 for room temperature potentials between -0.1v and 0.1v [10] for titanium-water systems. Multilayered scale with both Al_2O_3 and TiO_2 was found to form on Ti-6Al-4V samples that were oxidized in air at higher temperatures in a variety of environments [13]. Hydroxide films also form when the potential is reduced below -1.2 for the pH values between 7 and 10 [10]. For nickel base alloys, researchers have shown stable growth of Al_2O_3 and NiO oxide layers under varying potential and pH conditions [9,14,15]. In fact, researchers have used electrochemical techniques to process material surfaces for a variety of applications [9-12]. Although the anodic layer that forms on the surface adheres to the base material, it may be removed by mechanical polishing. However, the polishing media may be affected by the potential as well which can impact the colloidal silica and alumina often used in these solutions. Because the anodic layer is influenced by the electrochemical properties of the environment including the electrolyte bath, the kinetics of the protective layer may be controlled using an applied voltage. This provides a mechanism for controlling the formation of the passive films.

Chemical-mechanical polishing (CMP) has been applied to fabricate micro-electro-mechanical systems where wafer planarization is an important component [16]. The alkaline chemistry of the slurry is thought to hydrolyze the oxide surface and weaken the bonding. The mechanical polishing removes the weakened oxide layers and provides faster removal of features that rise higher above the wafer surface. CMP research with titanium has shown the interaction of the sample surface with copper ions within the slurry can further increase the overall removal rate of the titanium by oxidizing the titanium metal and forcing the titanium into the slurry. The copper that plates onto the surface is removed by mechanical polishing faster than the titanium [17]. This research further indicates the importance of the material surface and slurry interactions which strengthen or weaken the bonding energy of the oxide layers.

Although application of voltage during mechanical polishing has been previously suggested [18-20], the use of a potential applied strictly for the purpose of creating a protective film where surface damage is contained for subsequent removal offers an untested opportunity to combine the advantages of electrochemical passivation with the properties of chemical-mechanical polishing. The resultant process should have a faster removal rate than either technique alone, and produce a superior surface for characterization by reducing subsurface damage and precipitate pull-out that occurs during preparation. Since the overall preparation time is reduced, the procedure should also provide a more flat surface by reducing the surface rounding that occurs during long polishing steps.

The subsurface damage and overall image quality of samples are difficult to assess. One potential method takes into account the impact subsurface damage has on the analysis of diffraction patterns developed during EBSD. Samples with higher subsurface damage provide EBSD results with lower image quality (IQ) values as determined by automated software analysis. The values are determined by summing the detected diffraction peaks in the Hough Transform [21] and are therefore influenced by residual strain produced during sample processing. Unfortunately, the local alpha phase colony microstructures within Ti-6Al-4V samples impact the averaged IQ values, making it important to sample a large enough region that encompasses multiple colonies in order to compare results between titanium samples.

The objective of this research effort is to develop and test an electro-chemical-mechanical sample preparation technique (ECMP) for titanium and nickel base superalloys. Ti-6Al-4V and nickel 718 were used to test the approach. The technical goal is to limit the subsurface damage

within the passivation film layer which is subsequently removed by mechanical and electro-chemical polishing.

2. Methods and Procedures

2.1 System Design

The anodic behavior of nickel and titanium in the polishing solution was tested using a potential dynamic test system that tracked the potential difference of a 1 in² coupon immersed in the electrolyte solution (Allied 0.05 colloidal silica solution mixed with an equal part of distilled water). Sheet samples of both Ti-6Al-4V and IN100 were tested using a standard potential dynamic test rig by applying a current across the sample and measuring the potential in reference to a standard hydrogen potential probe. The samples were wiped with a Scotchbrite™ pad and cleaned with isopropyl alcohol prior to the test to remove oxide layers that may have formed. Each alloy system was tested multiple times over a range of electrical densities. The results provided voltage ranges to generate oxide layers within the room temperature electrolyte pH ranges.

An electro-chemical-mechanical system (ECMP) was constructed with a vibrating base plate and sample holders that were specifically designed to transfer potential only across the sample surface to the base (Figure 1). The ECMP consists of a power supply and feed-back system, a power distribution/wire harness assembly, sample holders, a chemical bath, and a vibrating base plate system.

The computer controlled power supply provides voltage to connection wires. The application of the voltage is controlled by a feedback system and software controlled operating system that regulates the power based upon the formation of the passivation film on the sample surface. The formation of the film changes the resistance of the system and impacts the measured current. A control system was developed using Labview™ software to allow pulsed voltage regulation and controlled feedback to evaluate passivation layer formation. A data acquisition card (NiPCI 6052E) and a terminal connection (BNC-2110) (both produced by National Labs™) are used in connection with a standard computer.

The voltage is transmitted through the connection wires to a power distribution plate (Ti-6Al-4V, 12" by 12" by 0.016" thick) and wire harness which allow multiple rotating samples to be connected in parallel. Nickel-plated acoustic wire (0.027" diameter) is used to connect the power distribution plate and the sample holders. The voltage is transmitted directly to the insulated holders where it is channeled to the back surface of the material sample. The holders are approximately 4.5 inches high, including the main conductive screw, and are constructed of a 316SS holder weight that sits upon a non-conductive polymer base (polyvinyl chloride). The base has an O-ring attached to the outer diameter to allow rotation and insulation against the metallic base plate. The sample is held in place within the holder base using teflon screws. The material sample is mounted in conductive mounting compound. A conductive threaded screw (main screw) with one hollow end connects components and transfers the applied voltage through the assembly and onto a flat head that the sample is held against. The threaded screw allows adjustment of the specimen height. The weight is not threaded but is held in-place by a 316SS nut that is connected to the main screw.

The holders rotate in an alkaline bath (Allied™ 0.05 colloidal silica solution mixed with an equal amount of distilled water) upon a polishing cloth. The holder base ensures the current

flows through the specimen face, through the alkaline bath, and into the base plate. The base plate vibrates to rotate the sample holder at an adjustable rate. The current across the specimen face is measured using a Fluke™ 8845A precision multimeter. The information is fed-back into the control system to optimize removal conditions.

The sample surface is modified as the current across the surface excites reactions between the surface material and the alkaline bath medium. As oxide layers develop or are impeded (depending on the applied potential), the alkaline bath chemistry is altered, and the sample surface changed as it rotates against the base plate and is mechanically polished by the suspended Si. By controlling the voltage and bath chemistry, the material surface is polished with the chemical reactions augmenting the mechanical polishing to reduce surface stress.

The system was tested under standard polishing conditions using the same sample holders and weights as with the ECMP, but without the applied voltage, to simulate traditional removal performance.

2.2 Experimental Procedures

Samples of Ti-6Al-4V and nickel 718 were cut from stock using a diamond saw and polished to a 3 micron finish using an automatic sample polishing system to reduce variability in preparation procedures. The samples were marked using a Vickers™ hardness tip loaded at 500 g and imaged to provide a depth measurement of the indent. The samples were run at different voltages and imaged to determine the change in the indent depth. The initial tests were run at low voltages and high voltages based on the earlier potential-dynamic results. The samples were tested at the optimum voltages under cyclic conditions where positive voltage was applied for a specific time, and then the negative voltage at the same absolute value was applied for the same time. This alternated the voltages applied to the sample and helped create and then remove the passivation layer forming on the sample surface. The polishing solution and cloth were replaced before every test, and the vibrational speed of the base plate for all conditions was maintained the same to reduce experimental variability. The depth of the indents was evaluated at 30 minute intervals for a variety of voltages up to 250 minutes.

Following the initial test for removal rates, titanium and nickel samples were re-tested at the optimum conditions and imaged using a Quanta™ FEI scanning electron microscope operating at 10 kV and a magnification of 300 times. For subsurface damage assessments, titanium and nickel samples were also evaluated using an XL30™ FEI scanning electron microscope equipped with an EBSD system operating at 20 kV, spot size 5, at a magnification of 350 times. The samples were evaluated during multiple runs with the resulting EBSD data stitched together using a Labview™ software program. The titanium sample was marked using a Vicker's™ indent with a 500g load and polished to a 3 micron finish. The sample was run for 60 minutes in the ECMP and evaluated using the EBSD system. The sample was then removed from the SEM and re-prepared starting with a 600 grit paper and polished down to a 3 micron finish as before. The sample was placed in the vibrating system and run for 250 minutes and evaluated using the same EBSD system and parameters, and using the indent to ensure the same general area was evaluated as before. The procedure was repeated for the nickel sample, only grid markers placed on the perimeter of the sample were used to locate the same region for EBSD analysis.

To further evaluate the quality of the subsurface of the processed sample TEM foils were prepared normal to the polished surface through focused ion beam (FIB) methods. Prior to

milling, the surface of the sample was carbon coated followed by platinum deposition to protect it from the ion beam milling away the surface layer. The sample was then analyzed with a Titan 80-300kV TEM. High resolution EELS spectrum profile was obtained across the sample in the STEM mode, with an aberration corrected sub-angstrom probe.

3. Results and Discussion

3.1 Removal Rates

The current density for the sample during the potential dynamic tests provided the starting ranges for optimizing removal conditions using the ECMP. Unfortunately, the mounting compound used in the experiment altered the true current density of the surface during the tests. This was compounded by the changing properties of the silica solution and the polishing cloth as the surface of the sample was polished.

Based on removal tests using constant applied voltages, the +0.08v condition provided the highest removal rate material (over 30 minute run time). Similarly, the nickel material at +5v voltage provided the highest removal rate (over 30 minute run time). The rates were measured by comparing the depth of the Vicker'sTM indent using optical microscopy. The removal rates reflected the generation of passivation layers followed by removal of the layers by mechanical polishing. Additional tests optimized the conditions by cycling the voltage. Cycling the voltage impeded oxide and hydride formation and accelerated the removal of the passivation layers by mechanical polishing. Figures 2 and 3 show removal rates obtained by alternating the applied voltage from positive to negative over a specific cycle rate. The results indicate that the +/- 0.08 v applied held for 210 seconds had the highest removal rate. For the nickel samples, the +/- 5 v applied voltage held for 90 seconds had the highest removal rate. Removal rates, based upon indent SEM measurements, were 187.5 nm for titanium and 250 nm for nickel for the 30 minute run time. The data confirms that the cyclic potential approach provided higher removal rates than either anodizing or the mechanical polishing without applied potential.

3.2 X-ray Photoelectron Spectroscopy (XPS) Analysis

The anodic layer was evaluated using X-ray photoelectron spectroscopy (XPS). A Ti-6Al-4V sample was polished to a 3 μ m finish and compared to two Ti-6Al-4V samples that were polished in the ECMP. The first of the two samples was polished to a 3 micron finish and placed in the electrolyte with a +0.08v potential applied for one hour. The second of the two samples was also polished to a 3 micron finish, but placed in the electrolyte with a -0.08v potential applied for one hour. The three samples were analyzed using a multi-sample stage.

The X-ray photoelectron spectroscopy (XPS) was performed on a Surface Science InstrumentsTM M-Probe using monochromatic Al K α X-rays (energy 1486.6 eV). Depth profile analyses were acquired by sputtering of the respective sample surfaces with an argon ion gun (1 keV, 10 mA, 6 Torr argon) for 20 seconds followed by data collection of the Ti 2p (448 – 470 eV) and O 1s (522 – 540 eV) regions for 15 seconds each. This cycle was repeated 20 times for a total sputtering time of 400 seconds. CasaXPSTM software was used for curve fitting and interpretation of XPS signals.

Observation of the Ti 2p region for the base and ECMP samples indicates the presence of an

oxidized titanium layer at each of the sample surfaces. Depth profile analysis through the oxidized layer into the underlying metal suggests that the oxidized layer is thicker in both of the ECMP samples. This trend can be visualized through observation of the Ti 2p^{3/2} peak in the spectral data found in Figure 4. The Ti 2p^{3/2} peak is initially observed at 458.4 eV indicating that titanium is present in its oxidized state. After controlled sputtering of the sample surface the Ti 2p^{3/2} peak gradually shifts to 453.7 eV representative of metallic titanium. In the base Ti64 samples this transition takes *ca.* 60 – 80 seconds of total sputtering time to completely move through the surface oxide layer. Sputtering times of *ca.* 180 – 200 and *ca.* 200 – 220 seconds are required to move through the oxide layer in the negative and positive electropolished samples, respectively. Under the described operating conditions a sputtering rate of *ca.* 0.1 nm is observed for a 10 nm SiO₂ standard, which suggests an approximate thickness of the oxide layer for the base sample to be 6 – 8 nm compared to an approximate thickness of 18 – 22 nm for the electropolished samples. Similar trends are observed for the O 1s spectral region (Figure 5) which demonstrates a significant loss of oxygen at the sample surface as sputtering time is increased. The results agree with the potential dynamic data reported earlier [10].

3.3 Electron Energy Loss Spectroscopy (EELS) Spectrum Profile Analysis

The STEM image in Figure 6 shows the region near the surface where the EELS line profile analysis was performed. The dark region near the surface of the sample was an artifact introduced possibly during the FIB process. Figure 6 shows the results from the EELS analysis performed on the sample. EELS spectra was obtained in the energy range 450 eV - 600 eV in order to observe the changes in Ti-L absorption edge. EELS spectra were continuously recorded at 1 nm intervals from the surface of the sample to the interior. Typical examples of the EELS spectra taken from the locations 1, 2 and 3 are illustrated in Figure 6. The spectra taken from the locations 1 and 2 show the Ti-L peak position at ~465 eV. On the other hand, the same Ti-L peak can now be seen at ~470 eV in the spectrum obtained near the surface at location 3. This shift of about 5 eV in the Ti-L peak position has been recorded up to a depth of 6-8 nm from the surface of the sample. This peak shift is indicative of O₂ near the surface. This is consistent with the results obtained from the XPS experiments mentioned above.

The dark region near the surface of the sample was closely examined for any hydride formation during the electrolytic process. Once again EELS line profile analysis was performed, now in the low-loss region (0-100 eV), to observe any changes in the plasmon peaks. The results are shown in Figure 7 for positions 1 and 2. An earlier study [22] has reported that the Titanium hydride formation can introduce a peak shift in the range of 5-8 eV in the plasmon peak position. No such shifts were seen in the spectra obtained. Hence it is suggested that the dark region is indeed an artifact in the sample.

3.4 Subsurface Damage

Surface damage was assessed using an EBSD system with evaluation of the resulting image quality (IQ) values. For the titanium and nickel alloys, analysis of the samples after 60 minutes in the system compared favorably to the samples processed without applied potential after 250 minutes. Although the samples for both polishing approaches still showed evidence of subsurface damage when viewed using the IQ maps, the values for grain orientation were above

acceptable limits for both (average IQ values were higher than 2000). For the titanium samples, the samples processed without applied potential provided an average image quality of 4117, compared to the value of 3920 for the sample processed using the $\pm 0.8\text{V}$, 210 sec cycle conditions. For the nickel samples, the sample processed with $\pm 5\text{V}$, 90 sec cycle conditions provided an average IQ value of 6875, compared to the value of 5255 obtained using no potential. Processing of the Ti and Ni samples with the ECMP for longer times further improved the IQ values.

4. Conclusions

The electro-chemical-mechanical system removed material from the titanium and nickel alloys at a higher rate than the chemical-mechanical system. The removal rate for both alloys was increased when the voltage was alternated and held for different lengths of time. The removal process produced a surface film that was removed by the mechanical action of the polishing medium.

An applied current in connection with the alkaline electrolyte produced an oxide layer on the surface of Ti-6Al-4V samples with a thickness approximately twice the thickness forming on the sample that was processed without applied current.

The EBSD results indicate lower surface and subsurface damage achieved using the electro-chemical-mechanical system for the titanium and nickel samples. The distribution of image quality values showed similar results from 1 hour processing using the electro-chemical-mechanical system compared with results after 2.5 hours of processing without an applied potential.

EELS and XPS analysis shows a shift in the energy absorption edges indicative of titanium oxide formation at the surface of the titanium sample. Further analysis did not find evidence of hydride formation at the interface.

5. Acknowledgements

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Figure Captions

Figure 1: Schematic of electro-chemical-mechanical polishing system with sample holder.

Figure 2: Titanium removal data for 0.08v constant and oscillating applied potential.

Figure 3: Nickel removal data for 5v constant and oscillating applied potential.

Figure 4: XPS binding energy (eV) versus sputtering time (sec) results for the Ti 2p peaks for the titanium samples, (a) unprocessed, (b) processed with negative potential. Sputtering conditions were identical.

Figure 5: XPS binding energy (eV) versus sputtering time (sec) results for the O1s peaks for the titanium samples, (a) unprocessed, (b) processed with negative potential. Sputtering conditions were identical.

Figure 6: A) STEM-HAADF image showing the region beneath the polished surface with positions 1, 2, and 3, and B) EELS spectrums obtained from the marked position 1, 3 in the sample show the relative shift in the Ti-L peak positions. Position 2 did not show any shift from position 1.

Figure 7: A) STEM-HAADF image showing the region beneath the polished surface with positions 1 and 2. B) EELS spectrums obtained from the marked position 1 and 2 in the sample show the plasmon peak positions. There was no shift in peak positions.

Figures

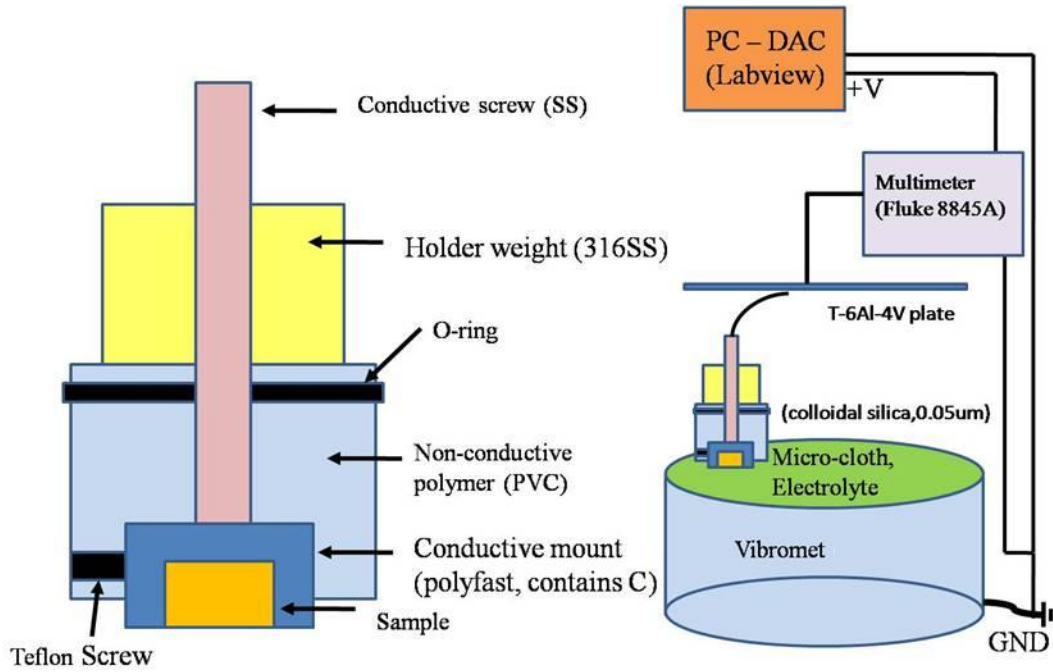


Figure 1.

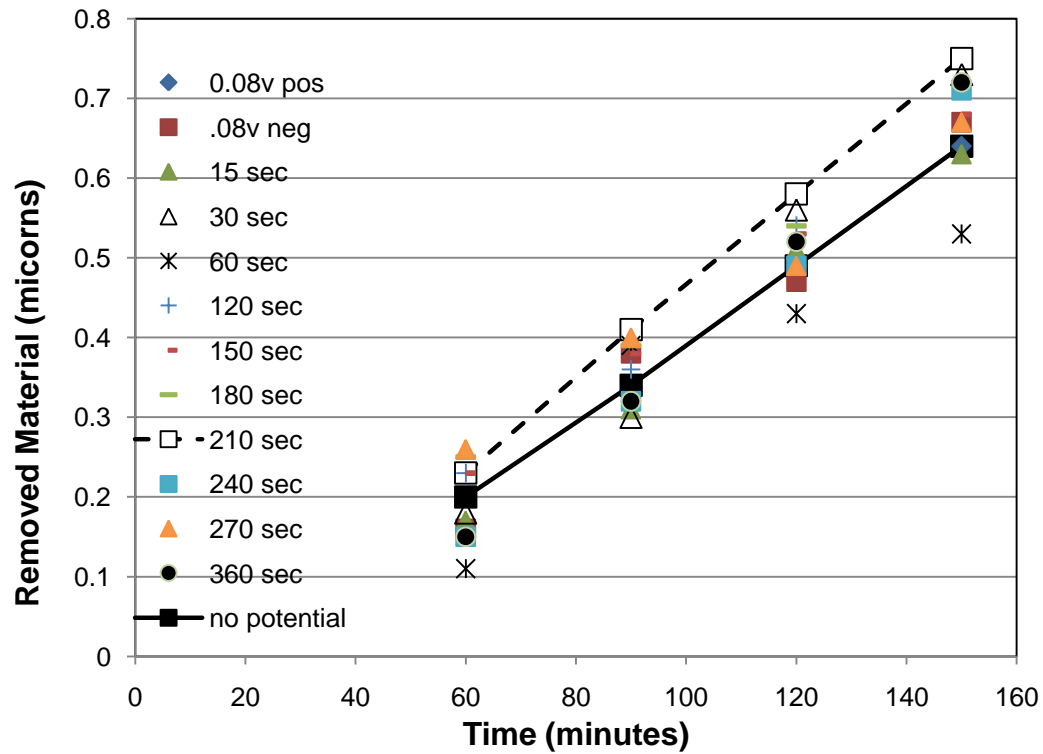


Figure 2.

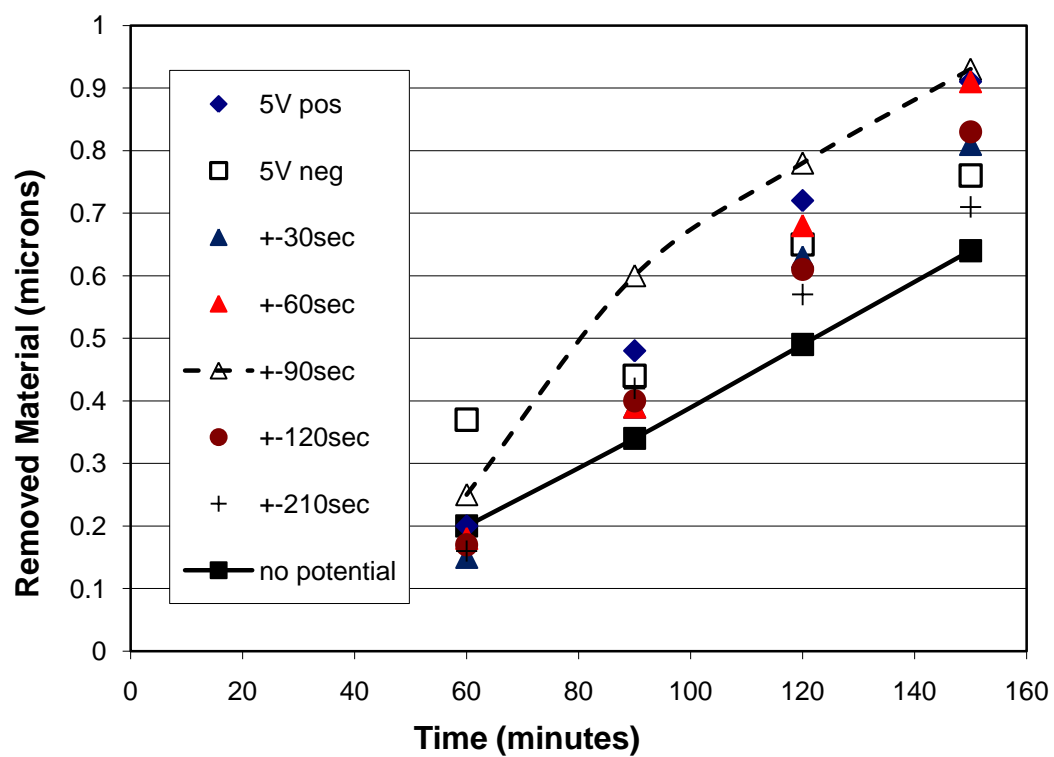


Figure 3.

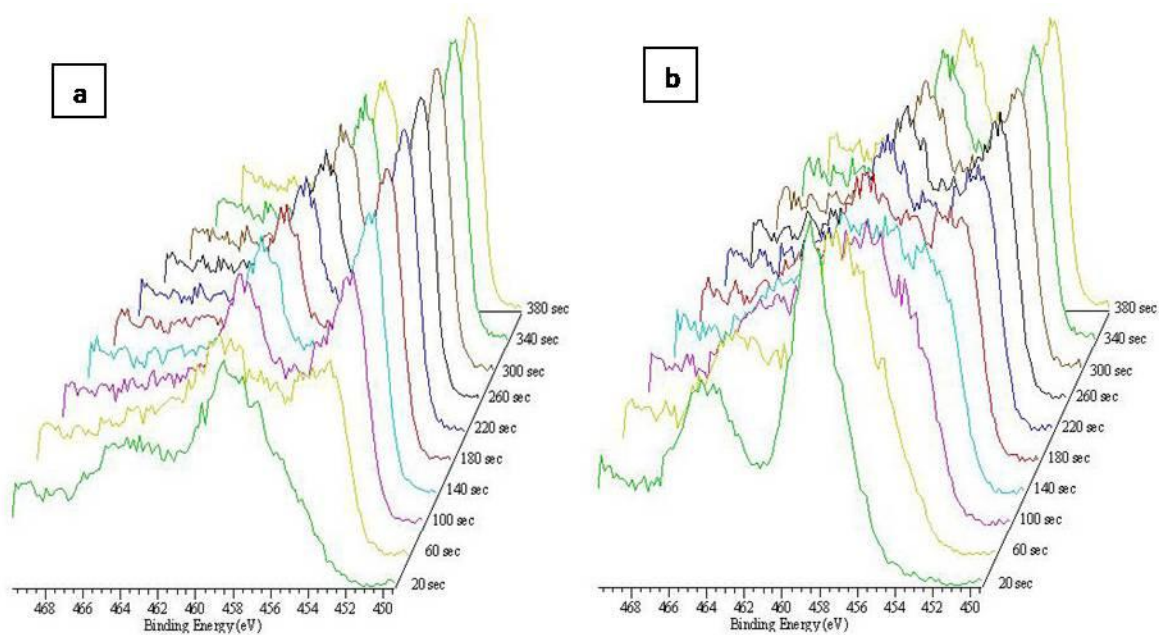


Figure 4.

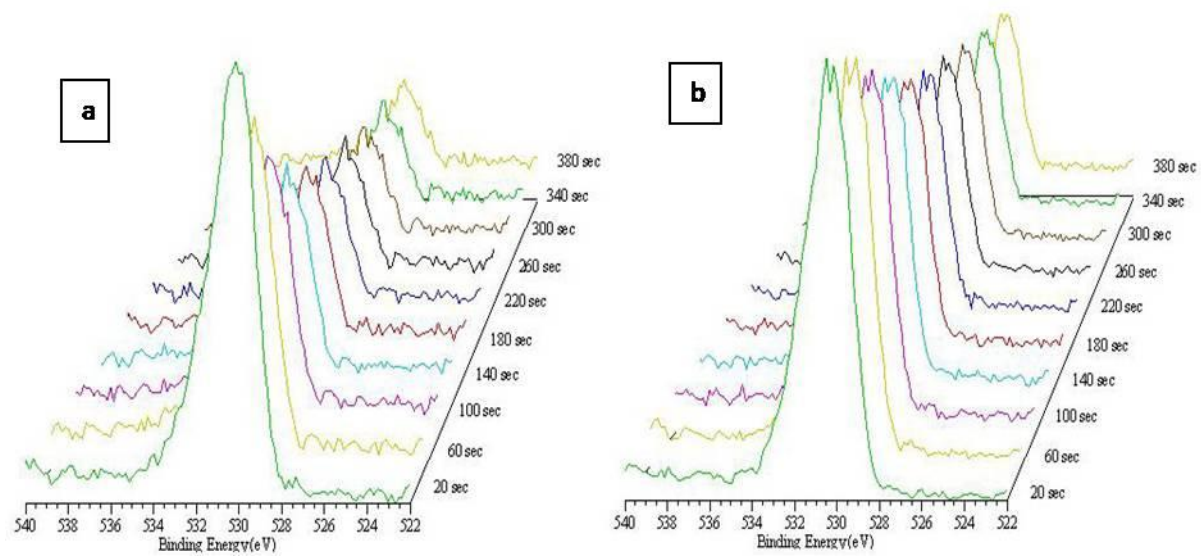


Figure 5.

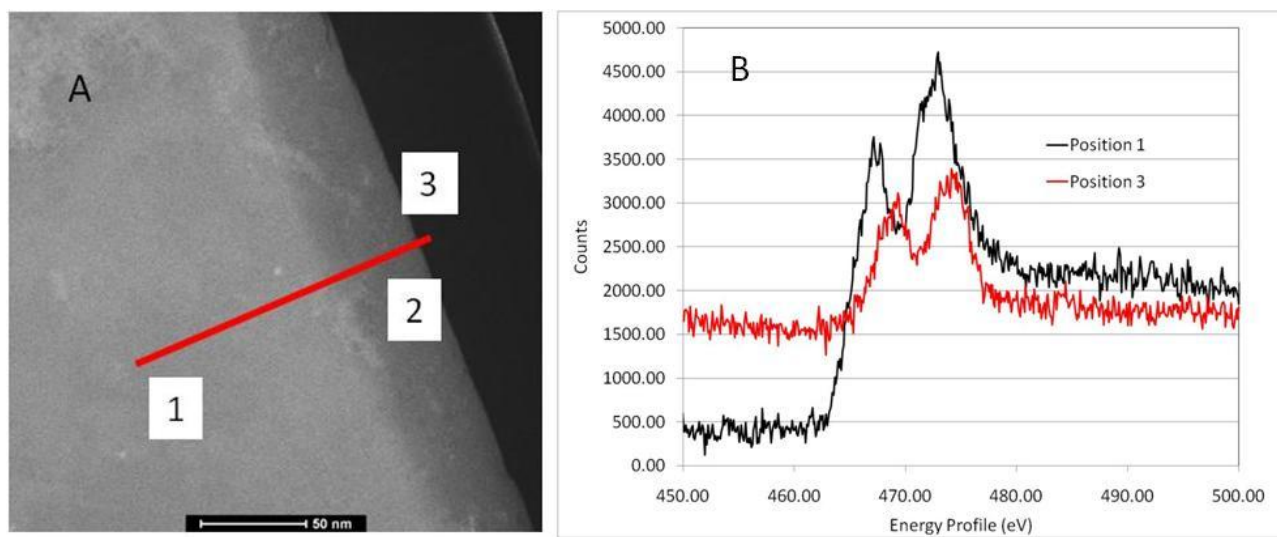


Figure 6.

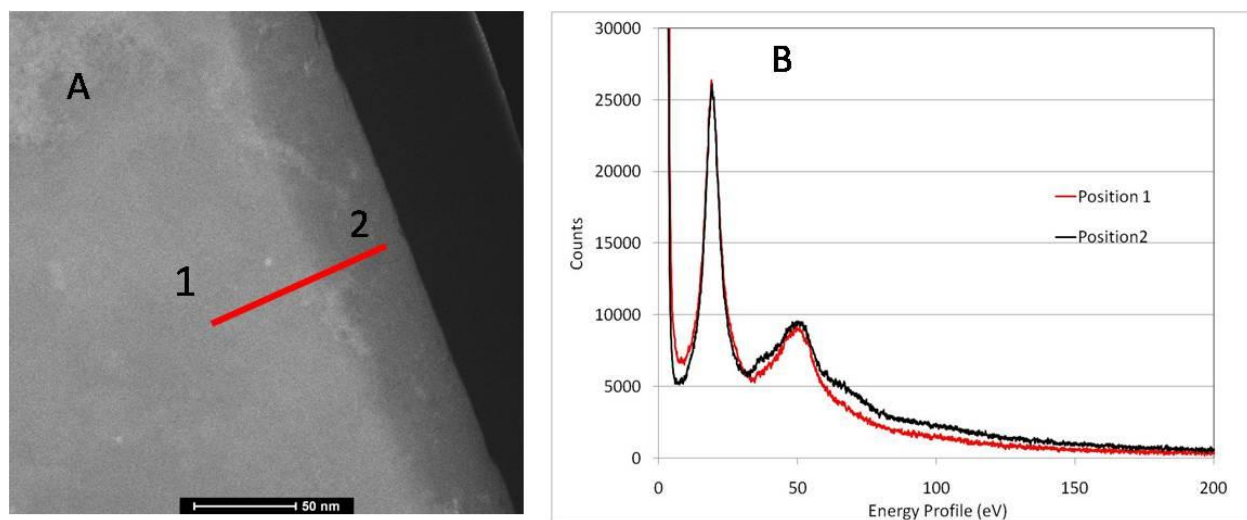


Figure 7.